ELECTROREDUCTION OF MANGANESE(II) CHLORIDE IN KCl-NaCl AND KCl-KF MELTS

Nodari Gasviani,[a] Gulnara Kipiani,[a] Shalva Andguladze[b] Marine Khutsishvili[a] and Nino Skhiladze[a]

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The electroreduction of manganese(II) chloride from chloride (NaCl-KCl) and fluoride-chloride (KCl-KF) melts has been studied in air atmosphere by polarography. In both melts, metallic manganese was obtained and the mechanism of the reduction of manganese(II)–ions was elucidated. Optimal parameters of the process could also be established.

* Corresponding Authors
Tel: +995 (032) 2 30 14 30
E-Mail: nodargasviani@mail.ru
[a] R. Agladze Institute of Inorganic Chemistry and Electrochemistry of Ivane Javakhishvili Tbilisi State University, Georgia, Tbilisi, Mindeli str. 11, 0186
[b] Georgian Technical University, Georgia, Tbilisi, Kostava str. 77, 0175

INTRODUCTION

Electrolytic preparation of metallic manganese and manganese alloys from melts and solutions has high industrial importance. Electrochemical preparation of metallic manganese from melts economically can only be competitive with the known electrochemical method based on aqueous or ionic liquid electrolyte solutions if the target compounds are special material like high-melting metal composites or alloys.[1,2]

EXPERIMENTAL

For the preparation of metallic manganese anhydrous $MnCl_2$ was used as a depolarizer. The experiments were carried out in the melts K, Na/Cl and K/Cl, F between 973 and 1023 K temperatures.

Voltammetric characteristics were taken using the potentiostat PI-50-1. Three electrode cell was used. A platinum wire was used as the cathode, glass-graphite crucible - as the anode and as the melt container. Platinum plate presented the reference electrode. The use of lead reference electrode was proved to be consistently unappropriated.

RESULTS AND DISCUSSION

The purity of KCl-NaCl was checked using voltammetry (Fig. 1). After addition of $MnCl_2$ to the melt KCl-NaCl (briefly over 1-2 minutes) only one wave occurs on the voltammogram (Fig. 1, curve 2), but after a period two additional waves appear (Fig. 1, curves 3, 4). The height of all three waves was nearly equal, the potentials were found to be -0.6÷ - 0.7, -0.78÷-1.0 and -1.1÷-1.3 V, respectively.

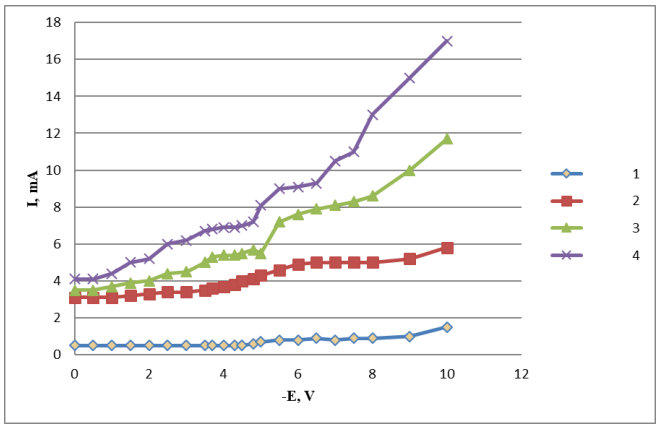

Figure 1. Voltammograms of electroreduction of manganese chloride in K,Na/Cl melt: 1-background, 2-background+$MnCl_2$ (0.2 wt.%), 3-background+$MnCl_2$ (0.6 wt. %), 4-background+$MnCl_2$(0.1 wt. %). Platinum as cathode and reference electrode, *T*=973 K

It is well known[3] that Mn(II) transforms into Mn(VI) ion melts due to oxidation with the oxygen content of the air

$$Mn^{II} \rightarrow Mn^{IV}+2e-$$

$$Mn^{IV} \rightarrow Mn^{VI}+2e-$$

The three waves observed on the voltammograms shows the three-step reduction of Mn(VI) to metallic manganese according to the following scheme:

$$Mn^{VI}+2e^- \rightarrow Mn^{IV} \quad \text{wave I}$$

$$Mn^{IV}+2e^- \rightarrow Mn^{II} \quad \text{wave II}$$

$$Mn^{II}+2e^- \rightarrow Mn \quad \text{wave III}$$

The electrolysis at the potentials corresponds to limiting currents of waves I and II did not produce any precipitate because the electrolysis products formed at the cathode (intermediate compounds) could re-dissolve in the electrolyte.

Table 1. Experimental and calculated data of the first stage of Mn(VI) electroreduction in the KCl-NaCl-$MnCl_2$ melt [$MnCl_2$]=2•10^{-5}mol cm^{-3}, *T*=973K.

V s^{-1}	E_p, V	$E_{p/2}$, V	$E_{p/2}$-E_p, V	E_p^a, V	E_p^c-E_p^a, V	$E_{1/2}$, V	$E_{1/2}$-E_p	Number of electrons calculated		
0.1	0.750	0.654	0.096	0.645	0.105	0.702	0.048	1.93	1.78	1.94
0.2	0.758	0.657	0.101	0.657	0.101	0.712	0.046	1.84	1.94	2.02
0.5	0.758	0.652	0.106	0.673	0.058	0.713	0.045	1.75	2.2	2.06
1	0.752	0.663	0.089	0.650	0.102	0.707	0.045	2.08	1.81	2.06
2	0.751	0.668	0.083	0.670	0.081	0.708	0.043	2.2	2.27	2.16

According to X-ray phase analysis, metallic manganese was obtained at the potential corresponding to the limiting current of wave III. All three stages were proved to be two-electron reduction processes. The analysis of the waves was carried out in semi-logarithmic coordinates **E**-lg(i_{lim}-*i*) and *E*-lg(i_{lim}/i_d-*i*).

The analysis of the wave I showed that the *E* - log(i_{lim}-*i*) relationship was linear. The process was reversible and may be described by the Kolthoff – Lingane[4] equation:

$$E = E_{1/2} + \frac{RT}{nF}\lg(i_d - i)$$

Comparison of the experimental and calculated data related to the process at wave I can be seen in Table 1. The number of the electrons was calculated by the following formulas[5]:

$$E_{p/2} - E_p = 2.2\frac{RT}{nF}$$

$$E_p^c - E_p^a = 2.2\frac{RT}{nF}$$

$$E_p - E_{1/2} = 1.1\frac{RT}{nF}$$

where

$E_{p/2}$, E_p, E_p^c and E_p^a are the potentials of half-peak, peak, cathode peak and anode peak potentials, respectively;

$E_{1/2}$ – potential of the half–wave (taken from stationary voltammetric characteristics,

n – the number of electrons.

As it can be seen from Table 1, the first stage is a two-electron reduction process.

The analysis of the wave II showed linear *E* – log (*i*/(i_{lim}-*i*) relationship, thus the wave can be described by the Heyrovsky-Ilkovich equation[5]

$$E = E_{1/2} - \frac{RT}{nF}\lg\frac{i}{i_{lim} - i}$$

The theoretical value of angle coefficient 2.303*RT*/*nF* at 973 K was found to be 0.036 at *n*=2, which is very close value to the experimentally found K_{ex} = 0.041 which confirms the presence of a two-electron reduction process.

The analysis of wave III unambiguously shows linear E - logi/i_{lim}-i relationship. The electrolysis at the potential corresponding to limiting current of this wave resulted in a solid product – metallic manganese. This process is irreversible.

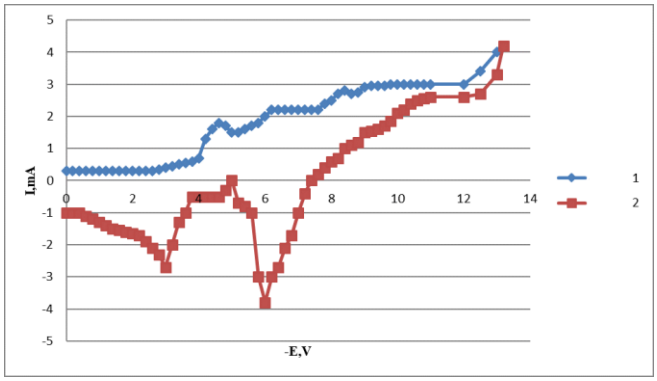

Figure 2. Cyclic voltammograms of Mn(VI) electroreduction. $MnCl_2$ (transforms into Mn(VI)) was added to the K,Na/Cl (I) melt in 0.6 wt. % amount, 1-cathodic curve, 2-anodic curve. Polarization rate was 0.1 V s^{-1}, *T*=973 K, platinum is a cathode

The cyclic voltammetric curves (Figure 2) showed the appearance of the process which is described by the Frumkin – Bagotski equation.[7]

$$\frac{\Delta E}{\Delta \lg\frac{i}{i_{lim} - i}} = 2.3\frac{RT}{\alpha n_\alpha}$$

To establish the effect of the background composition (in particular, of fluoride ions) on the electroreduction of manganese chloride some experiments were repeated in K//Cl,F melt. Replacement of chloride by chloride-fluoride mixture induced a change on the electroreduction curve of Mn(VI) (Figure 3).

In the K/Cl,F melt, at >0.4 wt.% manganese chloride content, two cathodic waves and one anodic peak could be fixed -0.95÷- 1.1, -1.4÷-1.5, and -1.08 V respectively (Fig. 4, curve 1 and 2).

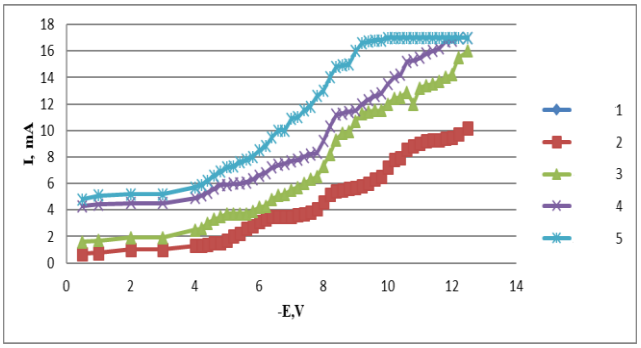

Figure 3. Voltammograms of Mn(VI) electroreduction. C_{MnCl2}=1.0 wt. %. Curves 1.4 were taken in KCl –NaCl melts at T = 973 K, curves 3.4 were taken in KCl –KF melt at T=1023 K. Polarization rate (V s^{-1}) was 0.1-2.3 and 0.5-4.5, respectively. Platinum was the cathode and platinum – oxygen was the reference electrode.

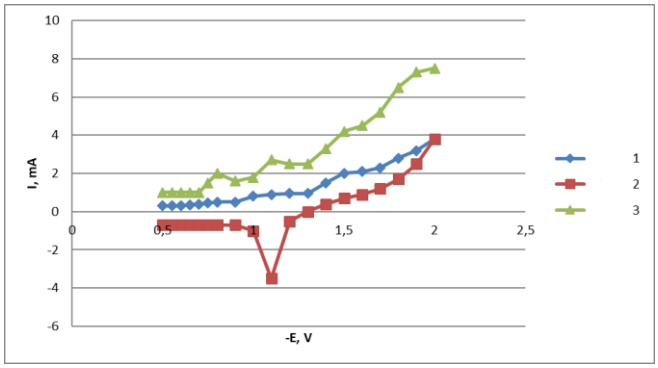

Figure 4. Voltammograms of Mn(VI) elecctroreduction. Background melt: KCl-KF. $MnCl_2$ (oxidized to Mn(VI)) was added in wt. %: 0.2 curves 1.2, 0.4 curve 3. Polarization rate was 0.2 V s^{-1}, platinum as anode, T=1023 K.

The peak heights were increased with increasing the polarization rate. At higher $MnCl_2$ concentration (C_{MnCl2}>0.4 wt. %) four waves of cathode reduction were observed at -0.65÷-0.75, -0.95÷-1.05 V, -1.3÷-1.5V and -1.55÷-1.65 V (Fig. 4, curve 3), respectively. Together with these, two pronounced peaks of anodic oxidation at E_a^{I}=-0.6 V and E_a^{II}=-1.05 V (Fig. 5), respectively, were occurred.

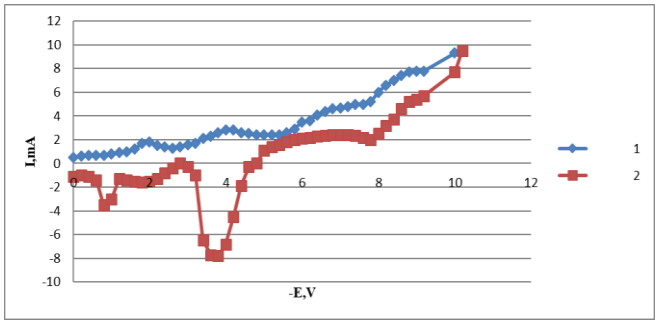

Figure 5. Cyclic voltammograms of Mn(VI) electroreduction in the K/Cl,F melt. C_{MnCl2}=1,0 wt. % 1. cathodic curve, 2-anodic curve. Polarization rate was 0.1 V s^{-1}, T=1023 K.

The first three waves correspond to Mn(VI) reductions observed in the pure chloride melt (shifted to the electronegative side) which might be explained with the formation of analogous mixed chloride – fluoride complexes of chlorides formed in pure chloride melt. The fourth wave in the range of -1.55÷-1.65 V belongs to a pure fluoride complex formed in the melt.

The large difference between anodic and cathodic peaks: E_c-E_a=0.7 V for the last stage shows the irreversible nature of the process (Fig 5). By potentiostatic electrolysis at the potential, corresponds to limiting current (1.7 V), metallic manganese was obtained. The analysis of the last stage of manganese chloride electroreduction in K/Cl,F melt showed that the wave could be described by Frumkin-Bagotski equation. The values of, αn_α calculated by experimental dependence were found to be 1.94÷2.1.

CONCLUSION

The composition of the background melt has considerable influence on the electroreduction of manganese chloride.[8] In the chloride melt in the presence of air the Mn–ions transform into Mn^{VI}. The electroreduction of Mn^{VI} occurs in three stages. First and second reversible stages are two-electron reduction processes without deposit formation at the cathode. The third stage results in metallic Mn formation, the process is irreversible.

The addition of KF into the chloride melt causes changes in the electroreduction process of $MnCl_2$ due to the formation of chloride-fluoride mixed and fluoride complexes. The discharge potentials are shifted to the negative side, and a new wave could be observed belong to the pure fluoride complex reduction. The preparation of metallic manganese can be performed from both melts (K, Na/Cl-$MnCl_2$ and K/Cl, F-$MnCl_2$).

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